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A SURVEY OF THE BEHAVIOR OF CARBON IN TUNGSTEN
AS REVEALED BY FIELD-ION MICROSCOPY

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REPORTS CONTROL NO. 3

A SURVEY OF THE BEHAVIOR OF CARBON IN TUNGSTEN AS
REVEALED BY FIELD ION MICROSCOPY

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ABSTRACT

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Field ion micrographs have been obtained from tungsten and tungsten carbon alloys which have been subjected to a variety of heat treatments. It has been found that carbon in tungsten stabilizes the formation of stacking faults. An estimate has been obtained for the binding energy of carbon to stacking faults in tungsten which is 1 ± 0.25 e.v., based on the minimum temperature for annealing out the stacking faults (3000°C). Surfaces in tungsten have a much higher binding energy for carbon based on the observation that stacking faults in tips of about 10^{-6} cm diameter can be annealed out at much lower temperatures. The true lattice solid solubility of carbon in tungsten is probably much smaller than previously reported. The field evaporation potential for carbon exceeds that for tungsten. It is orientation sensitive and greatest in the vicinity of the (100) poles at the surface.

Author

INTRODUCTION

The field ion microscope can be used to reveal the atomic structure of refractory metals.⁽¹⁾ One of the possible interesting problems allied with refractory metals is that of unravelling the effect of interstitial elements on the mechanical properties of body-centered cubic refractory metals such as tungsten. These interstitial elements, which are present in small concentrations, are believed to deleteriously affect the impact strength of tungsten but the precise mechanism is unknown. Indeed, even the limit of solid solubility of carbon in tungsten is open to question. Thus, it is desirable to know where the carbon atoms that enter the tungsten lattice reside; what is the limit of solid solubility of carbon in tungsten; and what is the interaction between carbon atoms and dislocations in tungsten. These questions are a sampling of the many that can be asked and which one may hope to answer through intelligent use of the field ion microscope. No previous field ion microscope investigation of carbon in tungsten has been reported. It is believed therefore that this investigation is the first of its kind.

The first problem one may seek to solve is the identification of the carbon atoms in the field ion micrographs. An obvious method is to vary the carbon

content of the specimens and then to observe whether any corresponding variation occurs in the field ion micrographs. In brief, this was the modus operandi of the present investigation.

EXPERIMENTAL PROCEDURE

A. Construction of Field Ion Microscope

For the purpose of this research a field ion microscope was built (Fig. 1), with a detachable horizontal screen, sealed to the main microscope chamber through "O"-rings. A tungsten loop, which holds the specimen, is held in place by two copper capillary tubes sealed to a cold finger. An f-0.95 lens camera with a close-up lens is used to take photographs of the ion pattern.

B. Detailed Procedure of Tip Formation

The specimen tips were prepared by electrolytic etching of the specimen wires, in a thin layer of IN. potassium hydroxide solution floating over carbon tetrachloride. The tip was always etched 1 m.m. or so beyond the point where it fractured during etching. This was done to dissolve away that part of the tip where it suffers mechanical deformation due to fracture.

C. Examination of Tip Structure

The tip is mounted in the field ion microscope, which then is evacuated to 10^{-7} - 10^{-8} torr. The system is then filled to approximately 2 torr with helium gas, which is leaked into the system through a heated vycor tube. The tip is cooled by pouring liquid nitrogen into

the central cold finger, subsequently a positive potential is slowly applied to the tip, until a pattern is obtained on the phosphor screen

At this point, the system is opened to the diffusion pump, to clean out the impurity gases which come off from the tip surface as a result of application of positive potential to the tip surface. Helium is again leaked into the system through the vycor diffusor tube until a good image is again obtained on the screen.

Detailed examination of the tip structure is undertaken by field evaporating layers of atoms from the tip surface, lowering the voltage and taking photographs of the pattern on AG-103 spectroscopic film.

SPECIMEN PREPARATION

Two starting grades of tungsten were used in this investigation: 1) Commercially pure grade (reportedly $99.97 \pm .02\%$) obtained as 2 mil diameter annealed wire from General Electric Company and called C.P. Tungsten hereafter. 2) Zone-refined tungsten (reputed to have a resistivity ratio at 78°K of 70,000 : 1) obtained as 10 mil diameter cold-drawn wire from Westinghouse Lamp Division, Bloomfield, N.J. 3) Carburized commercial purity grade tungsten obtained as about 10 mil diameter wire from Westinghouse Lamp Division, Bloomfield, N.J. The carburization is believed to have been carried out in graphite, induction heated.

The C.P. tungsten obtained from General Electric was also carburized at our laboratory by evaporating graphite onto a heated tungsten wire in vacuo. The tungsten wire was held at $1750 \pm 50^{\circ}\text{C}$ for 30 minutes.

Heat treatments were carried out on both wires and tips. The wire heat-treatments were carried out in an external furnace. The tip heat treatments were carried out insitu in the microscope.

RESULTS

1) Commercially Pure Tungsten (G.E.)

Figure 2 is a typical field ion micrograph of a tip produced from C.P. annealed tungsten wire. The (011) pole emanates from the center of the photograph and the tip radius is about 3×10^{-6} cm.

2) Zone-refined Tungsten (Westinghouse)

Figure 3 is a typical field ion micrograph of a tip produced from cold drawn zone refined tungsten wire which was annealed inside the microscope by flash heating to about 1400-1600°C for about 2 seconds. A rather large solid angle is encompassed in this picture. The (011) pole emanates from the center and four other 110 poles ((101), (101), (110) and (110)) intersect the visible tip surface. The tip radius is much larger than for Fig. 2 and is here about 6.5×10^{-6} cm. Many excess bright spots can also be seen centered about the (001) and (010) poles located at 12 and 6 o'clock respectively. As will be discussed later these extra bright spots are impurity atoms.

3) Carburized C.P. (Westinghouse) Tungsten

a) Figure 4a is a typical micrograph of a tip produced from the as-received carburized wire. The streaks shown there lie along (112) planes and do not disappear but remain as the surface atoms are removed by field ionization. The thickness of the streaks

varies from 1 to 10 atom layers. Note also that there is an absence of randomly spaced bright spots in the regions that do not contain the streaks and that the resolution is good in those regions. Further note that the topography of the surface is not spherical but saddle shaped with the symmetry plane of the saddle parallel to (112).

b) Figure 4b shows the same tip as in Figure 4a after annealing for 2-4 seconds in the approximate range 1400-1600°C and field evaporating off a few layers to obtain a regular surface. Note the absence of streaks and the large agglomeration of random bright spots about the (001) pole located in this pattern at about 10 o'clock. Also note the presence of lesser numbers of random bright spots elsewhere. These random bright spots are believed to be carbon atoms on the surface.

c) If the same material as in Figure 4a is annealed in the form of wire in the range 2600-2800°C for 35 seconds in a vacuum of 10^{-5} torr, then quenched by turning off the current and tips formed, ion micrographs appear as shown in Figures 5a and 5b. Most of the streaks lie parallel to the (112) planes with some parallel to the (123) planes. There are many more streaks than in the starting carburized C.P. tungsten.

d) Figure 6a shows the same materials as in Figure 4a, after tips are formed from this carburized C.P. (Westinghouse) tungsten which have been heated to about 2600-2800°C for 15 seconds in nitrogen and then quenched. Not as many additional streaks are present as found after a similar treatment as above with the exception of a nitrogen atmosphere in place of vacuum. Upon sufficient field evaporation, it is found that some of the streaks in Figure 6a disappear and are replaced by a uniform distribution of bright spots as shown in Figure 6b. With further field evaporation, the number of bright spots increases until a sudden flash is observed, after which there are many fewer bright spots as shown in Figure 6c.

e) If the carburized C.P. (Westinghouse) tungsten wire is heated to just below the melting point in a nitrogen atmosphere, quenched and tips formed, then the ion micrographs appear as in Figure 7. Note the complete absence of streaks and the large number of random white spots. The spots seem to be denser about the (100) planes and to lesser extent on the (112) planes.

f) If the carburized C.P. wire is heated to 1800°C and slowly cooled from this temperature the result shown in Figure 8 is obtained. The streaks seem to have condensed into "precipitates."

4) Carburized C.P. Tungsten (G.E.) which has been carburized by evaporation of graphite onto the heated wire held at about 1700-1800°C for 30 minutes and quenched by turning off the current appears after a tip is formed as shown in figure 9a. Note the presence of streaks, as well as some distortion in their vicinity. The streaks are parallel to the (021) zone axis. The surface topography is again distorted in the direction of the streaks.

Upon annealing the tip insitu at about 1400-1600°C for a few seconds and observation it is found that the streaks have disappeared as shown in Figure 9b. However, there are random bright spots centered about the (010) pole.

5) Zone Refined Tungsten (Westinghouse)

a) Tips formed from zone-refined tungsten wire which is heated to about 2700-2800°C for about 30 seconds in a vacuum of 10^{-5} torr and quenched appear as shown in Figure 10. An enormous solid angle is apparent in this micrograph. Note the absence of streaks. Although the pattern is fairly well resolved there are random bright spots.

b) Tips formed from zone-refined tungsten wire which was treated to 2700-2800°C in a nitrogen atmosphere for about 1 minute, then quenched reveal patterns as shown in Figure 11. Note the presence of only a single streak as compared to the large number found in carburized C.P. tungsten similarly treated. Compare Figure 6a

versus Figure 11. There appears to be a step at the single streak shown in Figure 11. Also, there are random bright spots with good atomic resolution along the intervening surface.

DISCUSSION OF RESULTS

There is little doubt that the extra bright spots that appear in the carburized specimens originate at carbon atoms. The evidence for this statement is as follows:

- a) These spots are relatively absent in the C.P. grade tungsten.
- b) Heat treatments which act to place carbon in solution increase the number of such spots.
- c) Heat treatments which act to take carbon out of solution (precipitate the carbon) decrease the number of such spots.
- d) The helium microscope acts to remove surface adsorbed gaseous impurities at and above imaging potentials and all the micrographs are of surfaces which have been subjected to the high fields associated with field ionization. The only surface adsorbed species that can remain after such a treatment is carbon. Ehrlich⁽²⁾ has found that nitrogen desorbs under similar circumstances and it, next to carbon, has the highest binding energy to the underlying tungsten.

The bright streaks that appear in the carburized material are believed to be stacking faults. This belief is based on the observation that the streak appears unchanged as atomic layers are removed one at a time and that no other possible interpretation appears to be able to account

for this observation. Ralph⁽³⁾ has given similar arguments for the interpretation of such streaks. Further, a crystallographic analysis shows these streaks to be parallel to the (112) planes. Stacking faults should preferentially occur on this plane according to Hirsch⁽⁴⁾ and have been observed on these planes by Nakayama et al.⁽⁵⁾

With the assumptions that the bright spots originate at or in the vicinity of carbon atoms and the bright streaks are stacking faults then the following deductions may be made:

1. The trap strength for carbon is greatest for a free surface, somewhat less for a stacking fault and least for the available sites in a perfect lattice in tungsten. In somewhat different language, the binding strength for carbon is greatest for a free surface, less for a stacking fault and least for a site in a perfect lattice. This situation is schematically illustrated in an energy level diagram given in Figure 12.

This deduction is based on the observations that the stacking faults in carburized C.P. tungsten tips disappear on annealing in the range 1400-1600°C with a concomitant increase in the number of individual carbon atoms on the surface of the tip (the carbon atoms adsorbed along the stacking faults readily migrate to the surface over short diffusion distances.) In the case of tips, where there is a

large surface to volume ratio the equilibration between surface and volume acts to remove most of the carbon in the interior. The same effect would be much smaller in larger diameter specimens and, in fact, the stacking faults in carburized wires cannot be made to disappear by similar heat treatments. If all the atoms on the surface of a tip were carbon atoms, this would correspond to a concentration in the tip of about 1 percent. Thus, the surface could effectively remove all the carbon in the tip interior for a sufficient binding energy decrement.

The stacking faults in the carburized wires can only be made to disappear upon heating to near the melting point, which is likely to be above 3000°C in these wires. Thus, carbon can only be placed into solution at the expense of the stacking faults above about 3000°C . The true solid solubility of carbon in the tungsten lattice is therefore likely to be much smaller than reported⁽⁶⁾ because of the likely presence of stacking fault sinks in the tungsten. That is, the measured total "solid solubility" of carbon in tungsten should depend upon the number of stacking fault sinks that may form under the influence of the carburizing atmosphere and the dislocation network insitu. This tentative conclusion however, has not been subject to experimental verification in this present study. It is sufficiently probable nevertheless to place in doubt the quantitative values for the solid solubility of carbon in tungsten

previously reported⁽⁶⁾. It is also in good accord with the absence of a Snoek internal friction peak in carburized tungsten.

An estimate can be made of the binding energy of carbon to stacking faults and this estimate is made in Appendix 1. The result is on the order of 1 e v, which is an appreciable binding energy. It certainly is a strong possibility that the brittle behavior of tungsten can be due to the strong interaction between interstitial impurities, such as carbon and dislocations.

2. The stacking faults are stabilized by the adsorption of carbon and are probably produced by the dissociation of dislocations. This tentative deduction is based on the following observations: There are many streaks of limited length that appear much brighter than the primary streak along which these super bright streaks lie. These streaks are visible at lower voltages than that at which the whole pattern is imaged. These secondary streaks are believed to be the sites of carbon atoms along the stacking faults. Also, it was observed that many additional streaks could be produced in a carburized wire quenched in a vacuum from about 2700°C and many fewer streaks in a similar wire quenched in nitrogen. It is believed that this observation can be interpreted as indicating that there was more time available for the carbon to adsorb during the vacuum quench in nitrogen. The possibility that the stacking faults are

produced by quenching alone is eliminated by the observations that no stacking faults are produced on quenching a carburized wire from above 3000°C or non carburized wires from 2700°C. On the other hand, the closeness of the streaks suggests either that the dislocation sources must be very close together as in a boundary or that the stacking faults catalyze the formation of additional stacking faults. In view of the limited time for a "series" process to operate it seems more likely that the "parallel" process of decomposition of a boundary to form such stacking faults is the operating mechanism. It should be possible to detect this process with the field ion microscope.

3. The field evaporation potential for carbon is greater than that for tungsten in the vicinity of the (100) poles at the surface. This inescapable conclusion is based on the results of this investigation.

SUMMARY

In answer to the questions raised in the Introduction, it can be said that the carbon atoms in solid tungsten at room temperature are most likely to reside in stacking faults and precipitates. Very few carbon atoms are likely to remain in solid solution. Further, the interaction between carbon atoms and dislocations in tungsten is exceptionally strong with an estimated binding energy of about 1 e.v. More quantitative information can be obtained from selectively designed field ion microscope investigations.

APPENDIX I

In the absence of carbon it appears that a stacking fault is unstable -- it disappears or is not present in C.P. tungsten. For a stacking fault to be stable it is necessary that the stacking fault energy be on the order of 10 ergs/cm². Let us suppose that in the absence of carbon the stacking fault energy is between 30 and 100 ergs/cm². Thus, by Gibbs Adsorption

$$\frac{d\gamma}{dx} = \frac{XSF}{X} n.k.T$$

and by statistical Mechanics $XSF \approx e^{+v/kT}$

where γ stacking fault energy

X concentration of carbon in lattice

XSF concentration of carbon in stacking fault

V binding energy of carbon to stacking fault

n number of atoms/unit area of stacking fault

Hence

$$\frac{d\gamma}{dx} = e^{+v/kT} nkT$$

$$\text{or } V = +kT \ln \left[\frac{(d\gamma/dX)}{nkT} \right]$$

Substituting numbers

$$\frac{30-10}{3 \cdot 10^{-3}} \leq \frac{d\gamma}{dx} \leq \frac{(100-10)}{3 \cdot 10^{-3}} \text{ ergs/cm}^2$$

$$n \approx 10^{15} \text{ /cm}^2$$

$$kT = 1.38 \times 10^{-16} \times 3300^\circ \text{ ergs}$$

and therefore $V \approx 1 \pm .25 \text{ e.v.}$

ACKNOWLEDGEMENTS

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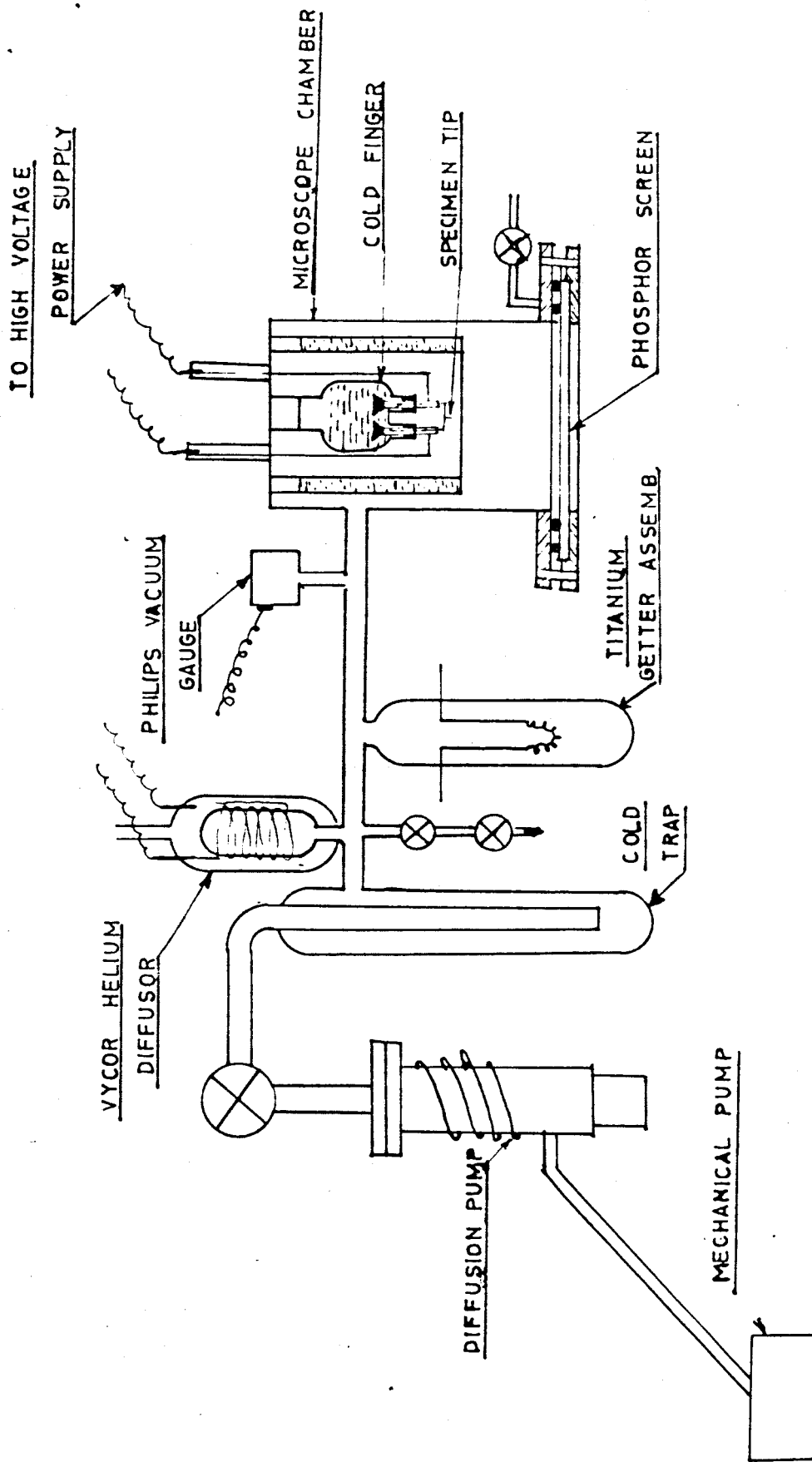


FIGURE 1 DIGRAM OF THE FIELD ION MICROSCOPE

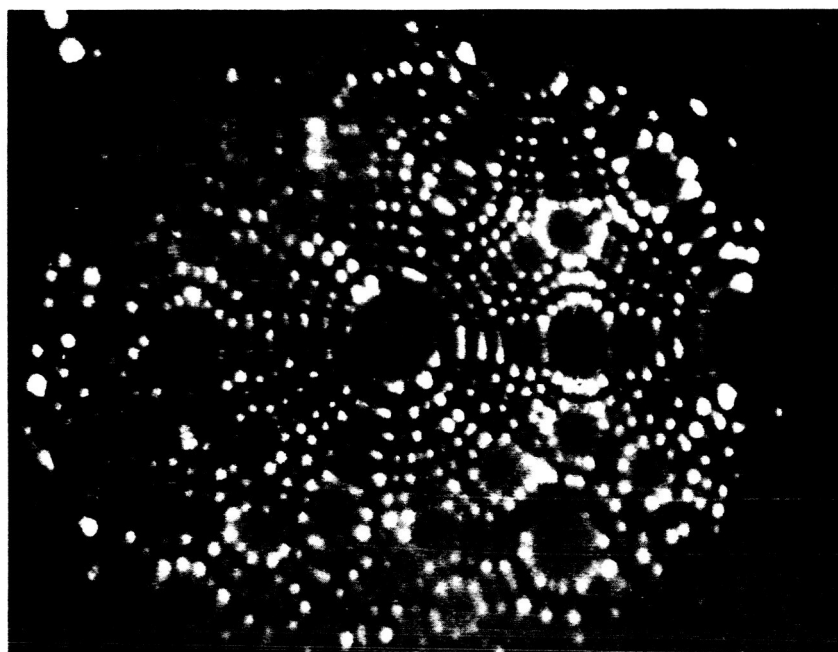


Fig. 2 - Commercially Pure Tungsten (Annealed state)

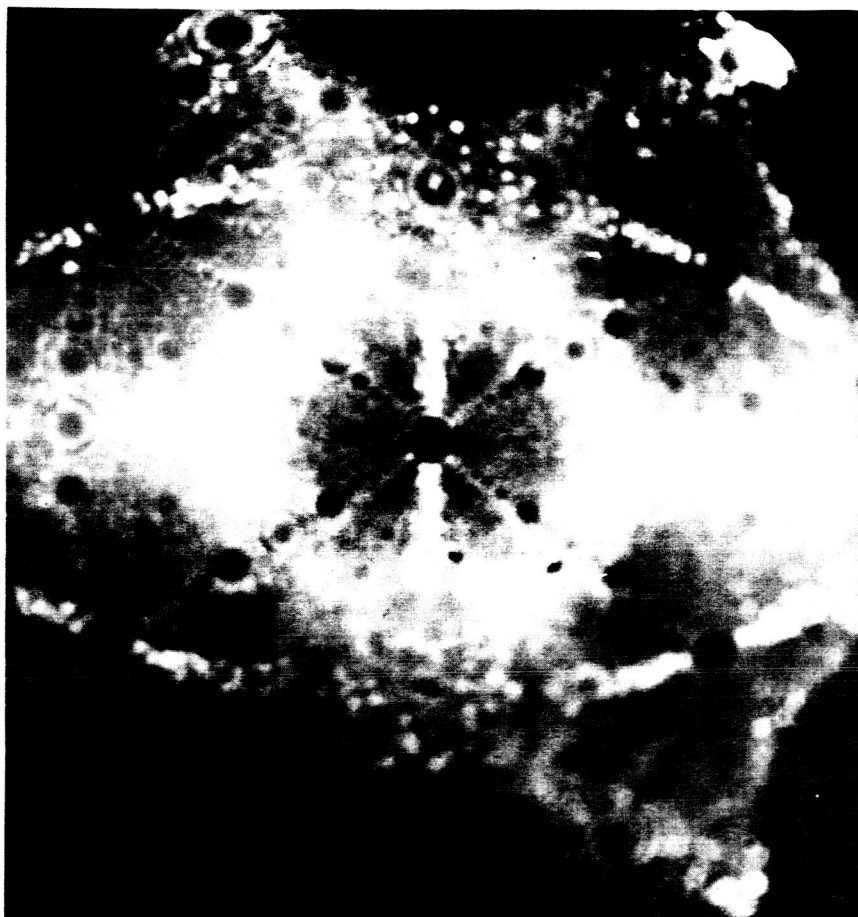


Fig. 3. Zone refined tungsten (cold drawn and annealed).

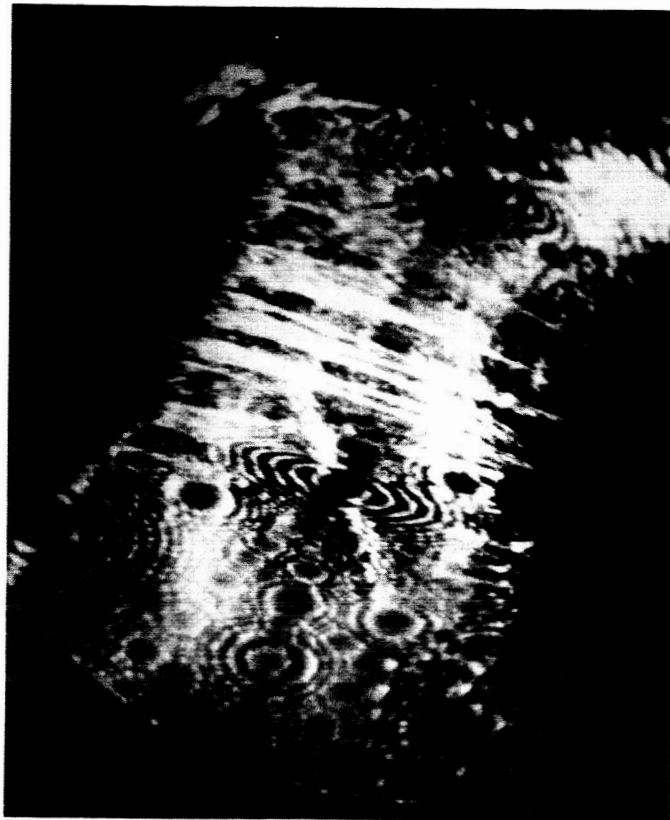


Fig. 4a. Carburized C.P. tungsten (as carburized at 1800°C).
Note stacking faults along (112) planes.



Fig. 4b. Same tip as in Fig. 4a after annealing between 1400-1600°C for 3 seconds inside the microscope. Bright streaks have disappeared.

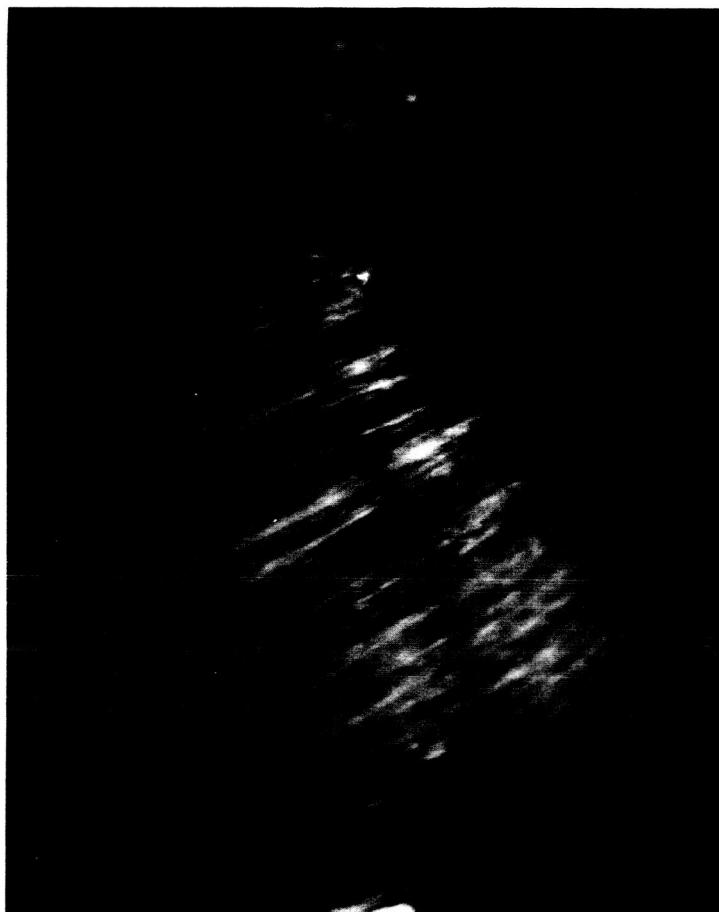


Fig. 5a. Carburized C.P. tungsten annealed as wire between 2600° - 2800°C in 10^{-5} torr pressure for 35 seconds and quenched.



Fig. 5b. Carburized C.P. tungsten annealed as wire between 2600°-2800°C in 10^{-5} torr pressure for 35 seconds and quenched.



Fig. 6a. Carburized C.P. tungsten annealed as wire between 2600° - 2800°C for 15 seconds in a nitrogen atmosphere and quenched.



Fig. 6b. Same tip as in Fig. 6a after partial field evaporation. Streaks have disappeared and a large number of bright spots appear.



Fig. 6c. Same tip as in Fig. 6b, after a sudden flash discharge. A large number of bright spots are removed.



Fig. 7. Carburized C.P. tungsten heated as wire below the melting point in a nitrogen atmosphere and quenched.

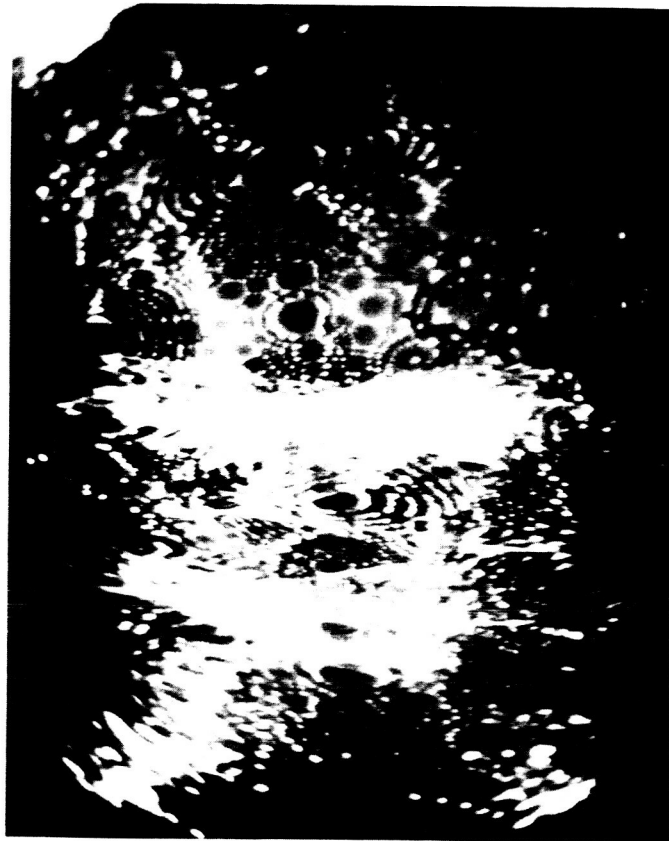


Fig. 8. Carburized C.P tungsten, slowly cooled from 1800°C, showing a precipitate.

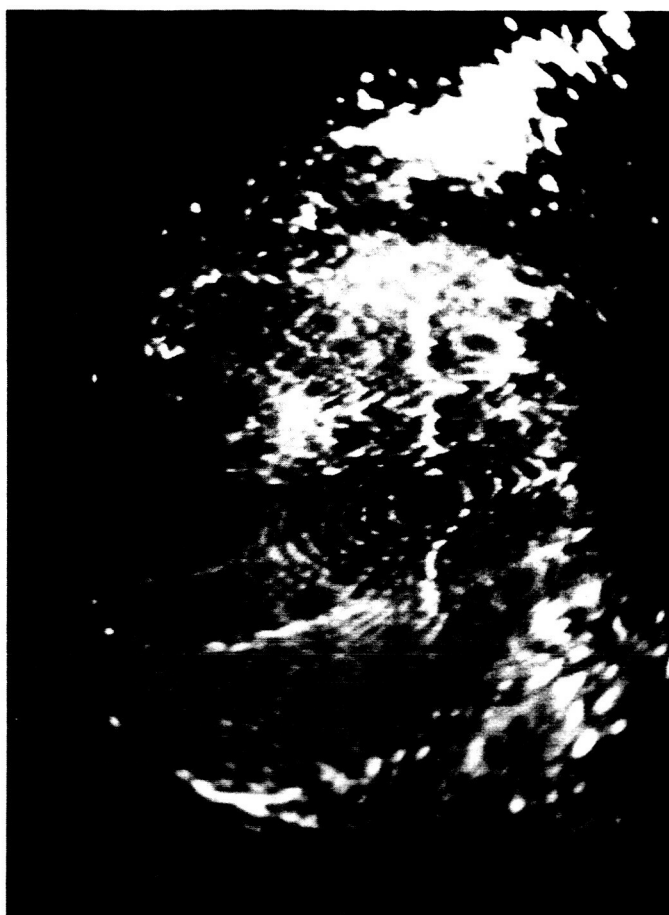


Fig. 9a. Commercially pure tungsten, carburized by evaporating graphite onto a heated tungsten wire held at about 1700° - 1800°C and quenched in a vacuum.



Fig. 9b. Same tip as in Fig. 9a after annealing between 1400°C - 1600°C for a few seconds inside the microscope. Streaks have disappeared.

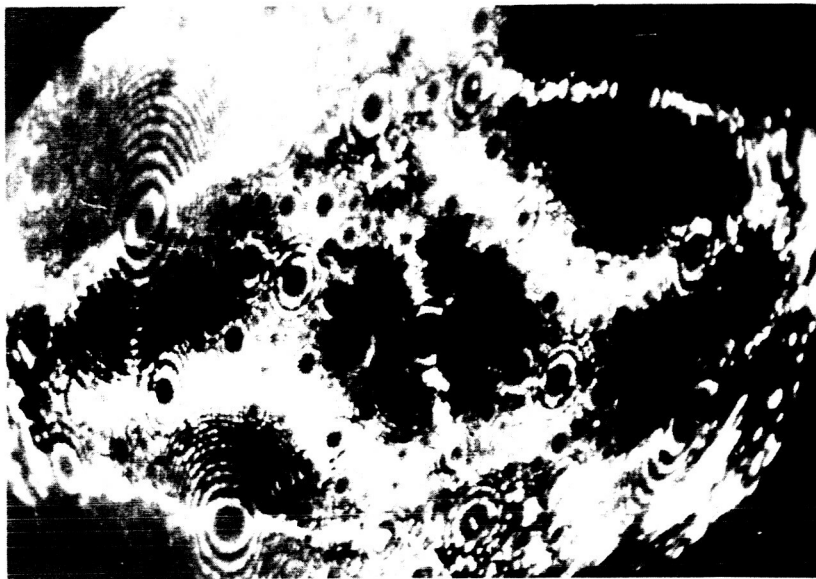


Fig. 10. Zone refined tungsten heated to approximately 2700° - 2800°C for about 31 seconds in vacuum and quenched.

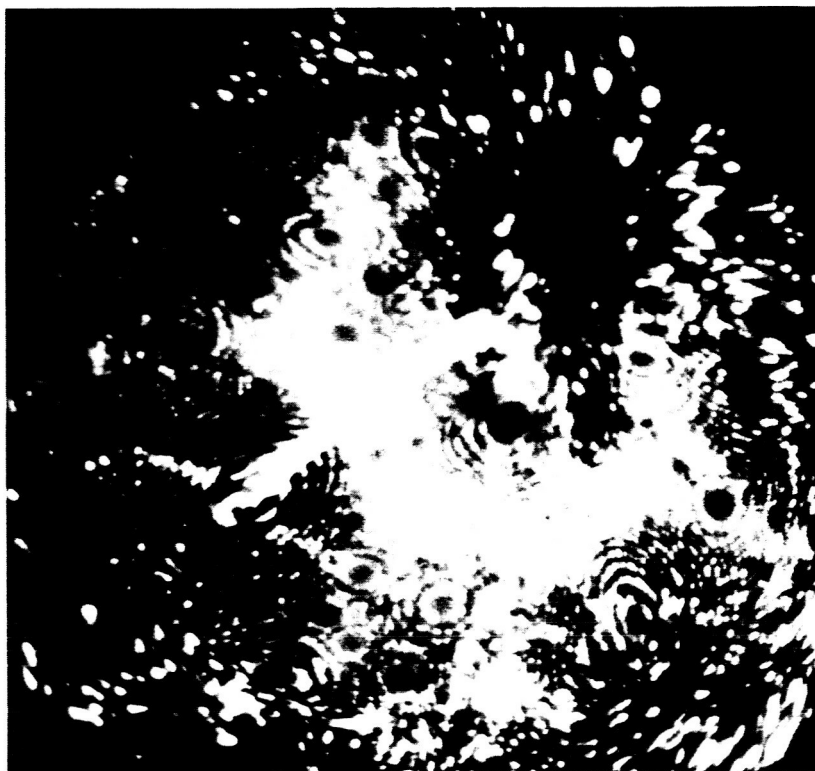


Fig. 11. Zone refined tungsten heated to about 2700° - 2800°C for about 60 seconds in nitrogen atmosphere and quenched.

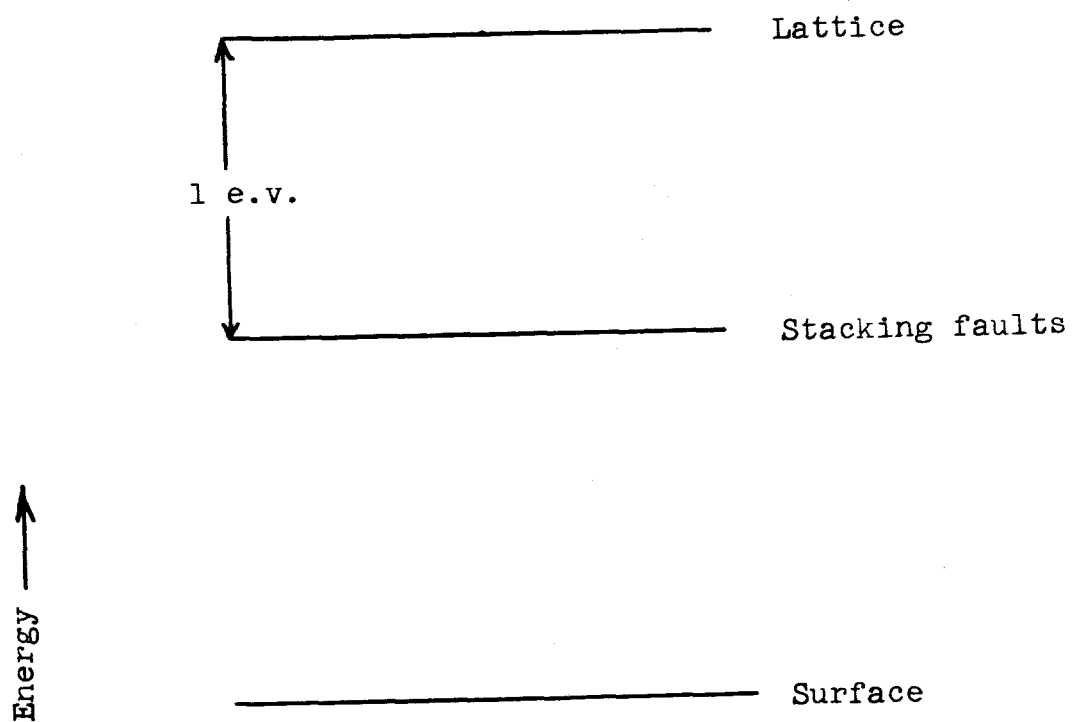


Fig. 12 - Energy level of carbon in tungsten